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ACIDOLYSIS OF POLY(4-METHYL-13-DIOXOLANE)(U)  
MASSACHUSETTS UNIV AMHERST DEPT OF POLYMER SCIENCE AND  
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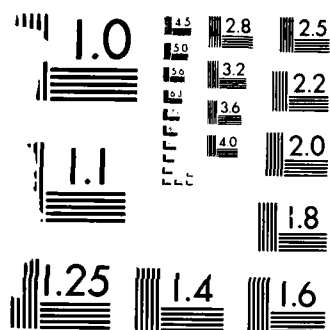
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Acidolysis of Poly(4-methyl-1,3-dioxolane)

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### Acidolysis of Poly(4-methyl-1,3-dioxolane)

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### Synopsis

The onset of decomposition of poly(4-methyl-1,3-dioxolane) was lowered from 70° by 0.1 weight % p-toluene sulfuric acid to 170° producing more than 81% yield of monomer. Protonation forms cyclic oxonium ion followed by depolymerization. Minor products are isomers of hydroxymethyl-2-hydroxyl-2-methyl ethyl ether and bis(2-hydroxyl-2-methyl ethoxyl)methane rearrangements of the oxonium ions. The first order rate constant of acidolysis of poly(4-methyl-1,3-dioxolane) is ca. 8.5 kcal/mole<sup>-1</sup> which is much smaller than about 17 kcal/mole<sup>-1</sup> for the acidolysis of poly(1,3-dioxolane).

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### INTRODUCTION

There are two types of polymers, both having either oxygen in the backbone, which are prone to depolymerization. They are polymers derived from aldehydes and from oxygen heterocyclic monomers. This property can be utilized to great advantage such as in E-beam microelectronic lithography. We have undertaken a systematic study of degradation of these polymers.

It is generally accepted that the polymerizability of acyclic compounds and conversely the depolymerizability of its polymer depends not only on the ring size, but also on the kind, number of position of substituents attached to the ring. There are many works on the polymerization of 1,3-dioxolane. Binet and Leonard<sup>1</sup> reported its equilibrium bulk polymerization making allowances for the non-ideality of the reaction. They obtained the following thermodynamic parameters for polymerization:  $\Delta H_{1c} = -4.2 \text{ kcal mole}^{-1}$  and  $\Delta S_{1c}^{\circ} = -11.4 \text{ e.u.}$ , Kumparenko et al.<sup>2</sup> reported the kinetics of thermal and acid degradation of poly(1,3-dioxolane) (PDO). The latter was studied between 140° - 200° while the thermal processes were investigated from 160° to 310°.

Okada et al.<sup>3</sup> first observed that 4-methyl-1,3-dioxolane polymerizes cationically to low molecular weight polymers. It polymerizes much more slowly than that of unsubstituted 1,3-dioxolane. The poly(4-methyl-1,3-dioxolane) (PMDO) has a skewed distribution. Using methylene chloride and light petroleum as a solvent-precipitant pair, Okada et al.<sup>4</sup> separated PMDO into a soluble and an insoluble fraction with MW 1,000 - 3,000 and 7,000 - 12,000, respectively. These authors found  $\Delta H_{1c} = -3.2 \text{ kcal mole}^{-1}$  and  $\Delta S_{1c}^{\circ} = -11.4 \text{ e.u.}$  for polymerization of MDO. Therefore, PMDO should undergo acid

catalyzed depolymerization much more readily than PDO. There have been no reports on this reaction.

The central purpose of this work is to study the kinetics, identify the products and elucidate the mechanism of acid induced depolymerization of PMDO.

### EXPERIMENTAL SECTION

#### Materials

Paraformaldehyde and 1,2-propandiol were obtained from Aldrich and used without further purification. *p*-Toluene sulfonic acid was crystallized from anhydrous methanol and vacuum dried at 50°.

The general method of Astle *et al.*,<sup>5</sup> in which excess of diol minimizes loss of volatile aldehyde was used to prepared MDO. 1,2-Propanediol (3 eq.) and paraformaldehyde (2 eq.) were heated with air-dried, regenerated Dowex-50 cation exchange resin (5 g for each mole of total reactants). Product was distilled as it formed as a water azeotrope until distillate temperature reached 90°. At this point more reactants (a 1:1 mixture) were added and the reaction was continued. The dioxolane and water layers were separated in a separatory funnel, and the dioxolane layer was dried with two portions of solid potassium hydroxide. Pure, dry 4-methyl-1,3-dioxolane was obtained by distillation from sodium at 1 atm., bp 83 - 83.5° (lit. 83.7 - 84.2°,<sup>6</sup> 85-86°<sup>4</sup>).

#### Polymerization

Polymerization of 4-methyl-1,3-dioxolane using  $\text{ZnCl}_2$ /acetyl chloride,<sup>3</sup> acetic anhydride/ $\text{HCIO}_4$ ,<sup>3</sup>  $\text{BF}_3 \cdot \text{OEt}_2$ ,<sup>4</sup> and  $\text{BF}_3 \cdot \text{OEt}_2$  in  $\text{CH}_2\text{Cl}_2$ <sup>7</sup> has been reported. We have found bulk polymerization at -78°, using trifluoromethane sulfonic

acid to be the best method. A typical example is described below. MDO (160 g, 1.82 mole) and trifluoromethane sulfonic acid (3.4 g, 0.046 mole) were mixed at 10° and charged into a dry reactor tube which was sealed with a rubber stopper wrapped with Parafilm. The tube was held in a dry-ice/acetone bath for two days. The cold tube was then broken and its contents allowed to fall into a mixture of trimethylamine (2 eq.) in 480 mL toluene precooled to 0°. The final temperature was -8°. The toluene solution was washed with 1 eq. potassium hydroxide in 160 mL water at 80° and finally with three 160 mL portions of water at 80°. Toluene/water azeotrope was then distilled (1 atm) followed by distillation of the remaining toluene at reduced pressure. Trace amounts of toluene were removed under high vacuum. The polymer was obtained as a clear viscous liquid, 120 g (75%).  $\bar{M}_n$  as estimated by determination of active hydrogen was 9,200. An infrared spectrum exhibited the expected weak bands at 3600 and 3500  $\text{cm}^{-1}$  for terminal OH groups as well as a weak band for a carbonyl impurity at 1730  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum was in accord with that reported by Firat and Plesch.<sup>7</sup>

#### Preparative-scale sulfuric acid-catalyzed decomposition

PMDO (22.5 g) was added dropwise to 0.5 g conc. sulfuric acid in a reaction chamber maintained at 10 mm in a 150° oil bath. A stream of nitrogen was maintained through the apparatus to remove volatile products which were trapped downstream with a water-cooled condenser followed two dry-ice/ethanol traps. After decomposition, 0.25 g brown tan remained in the reactor, 0.2 g brown liquid was formed in the condenser and 0.25 g light-brown liquid in the receiver below the condenser while, the majority of product was isolated from the traps as a clear colorless liquid (19.3g). Analysis by GC, IR and  $^1\text{H}$  NMR

showed that the major product was MDO. GC analysis was conducted on 3% QE-1 column and the FID detector response to authentic MDO was demonstrated to be linear. MDO content of the product from the traps was measured as 95.3%.

#### Instrumentation methods

Thermogravimetric analysis (TGA) was made with a Perkin-Elmer System 4 thermobalance. The polymer sample (ca. 10 mg) was heated at  $20^{\circ} \text{ min}^{-1}$  under a nitrogen flow of  $70 \text{ ml min}^{-1}$ . The sample holder was a  $10 \times 5 \times 1.5 \text{ mm}$  boat; the thermocouple was placed within 1 mm of the holder.

Gel permeation chromatography (GPC) was performed on solutions of 10 mg of PMDO in 20 ml of THF filtered through  $0.47 \mu$  pore filter paper with a Waters Associates 201 instrument equipped with five  $\mu$ -styrogel columns of  $10^2$ ,  $10^3$ ,  $10^4$ ,  $10^5$  and  $10^6 \text{ \AA}$  sizes.

The degradation products were analyzed with a Hewlett-Packard 5840 GC with fused quartz capillary column of  $20 \text{ m} \times 0.33 \text{ mm}$  coated with methyl silicone. The GC is interfaced with a Hewlett-Packard 5895 A mass spectrometer.

### RESULTS

#### Thermogravimetry

TGA reveals clearly that degradation of PMDO is catalyzed by *p*-toluene sulfonic acid. The curves in Figure 1 show that the initial decomposition temperature is lowered from ca.  $70^{\circ}$  to ca.  $170^{\circ}$  by 0.1 weight % *p*-toluene sulfonic acid. Derivative curves reveal that thermal degradation is a one stage process with the maximum rate of weight loss at  $300^{\circ}$ . In the presence of acid, weight loss is a two-stage process with weight loss maxima at  $100^{\circ}$  and  $225^{\circ}$ .

Fig. 1



### Variation of MW during degradation

The acidolysis of PMDO occurs at an appreciable rate at room temperatures. Ten mg of PMDO with 1 wt % of TSA were reacted under vacuum for various times. The wt % loss was determined and the  $\bar{M}_n$  of the polymer remaining was analyzed by GPC. The GPC curves are shown in Figures 2 and 3 and Table I lists the wt % loss  $\bar{M}_n$  values.

Fig. 2  
Fig. 3  
Table I

Table I

#### Acidolysis of Poly(4-methyl-1,3-dioxolane)

Time, min.	% wt loss	$\bar{M}_n \times 10^{-3}$
0	0	14.3
15	1.1	7.0
30	1.5	6.0
45	2.6	5.0
60	3.4	4.0
90	7.5	2.8
120	13	2.2
150	17	2.0
180	19	1.7
210	22	1.6
1440	23	1.1

The polydispersity  $\overline{M}_w/\overline{M}_n$  of the PDMO before and after acidolysis is about equal to the most probable distribution. Because the GPC column was not calibrated with known standards of PMDO and polystyrene universal calibration curve was used, the calculated  $\overline{M}_n$  values have relative significance but unknown accuracy.

PDMO was also isothermally decomposed at various temperatures by heating at a rate of  $10^\circ \text{ min}^{-1}$  to the desired temperature and held there for 60 min.

Table II The results are given in Table II in first order rate constants.

Table II

First order rate constant for the acidolysis of PDMO

Temp. °C	$k \times 10^5, \text{ sec}^{-1}$
25	0.96
70	4.5
80	7.6
90	11.3
100	15.6

#### Products of acid-catalyzed degradation

Preparative scale degradation at  $150^\circ$  and 10 torr in the presence of sulfuric acid gave volatile products at a high yield of 85%. The major component of which, 95%, was identified as the monomer MDO by GC (peak 1 of Fig. 4) infrared, and  $^1\text{H}$  NMR measurements. Thus the isolated yield of monomer

is 81%; the actual yield may be higher owing to the possibility of incomplete trapping.

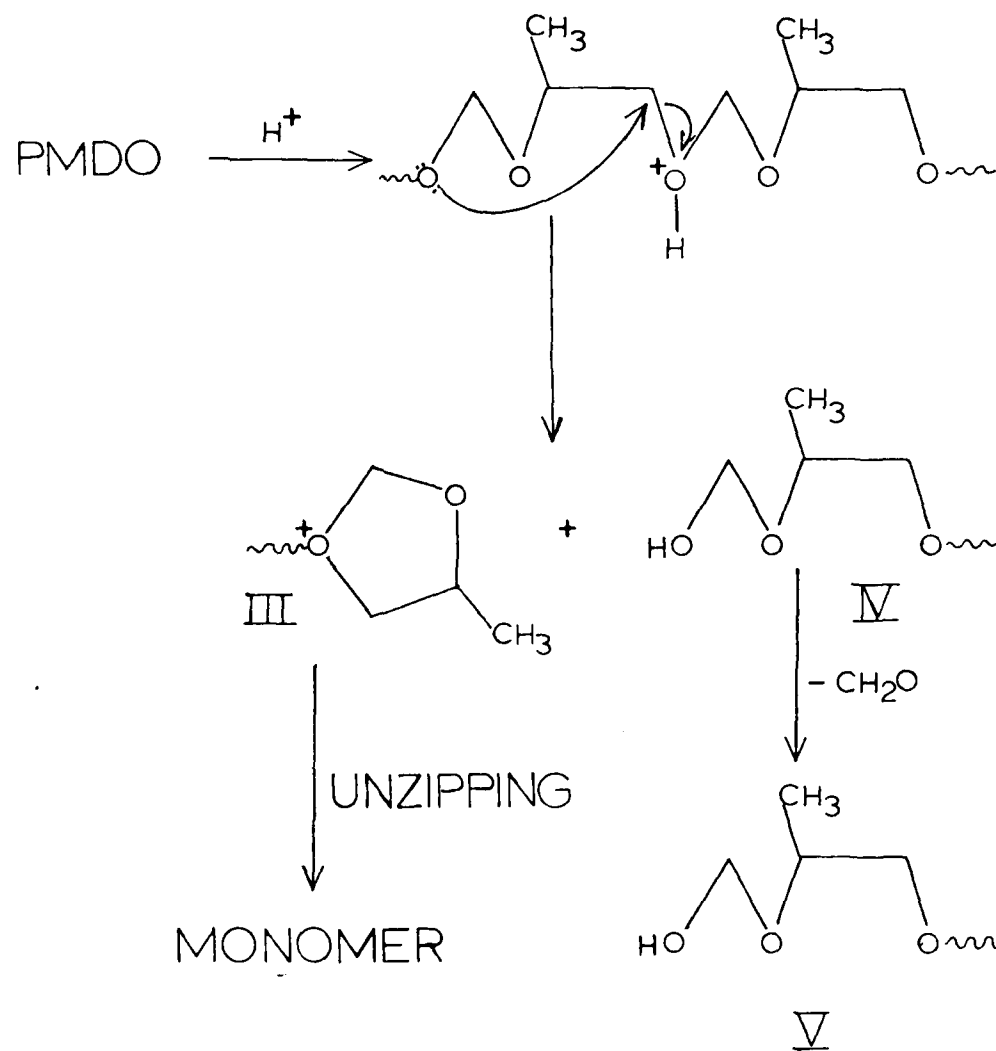
The other minor products were also identified by the above techniques. Peaks 2 and 3 of Figure 4 are isomers of hydroxymethyl-2-hydroxyl-2-methyl ethyl ether (I) and peaks 4, 5 and 6 are isomers of bis(2-hydroxyl-2-methylethoxy) methane (II).

#### DISCUSSION OF RESULTS

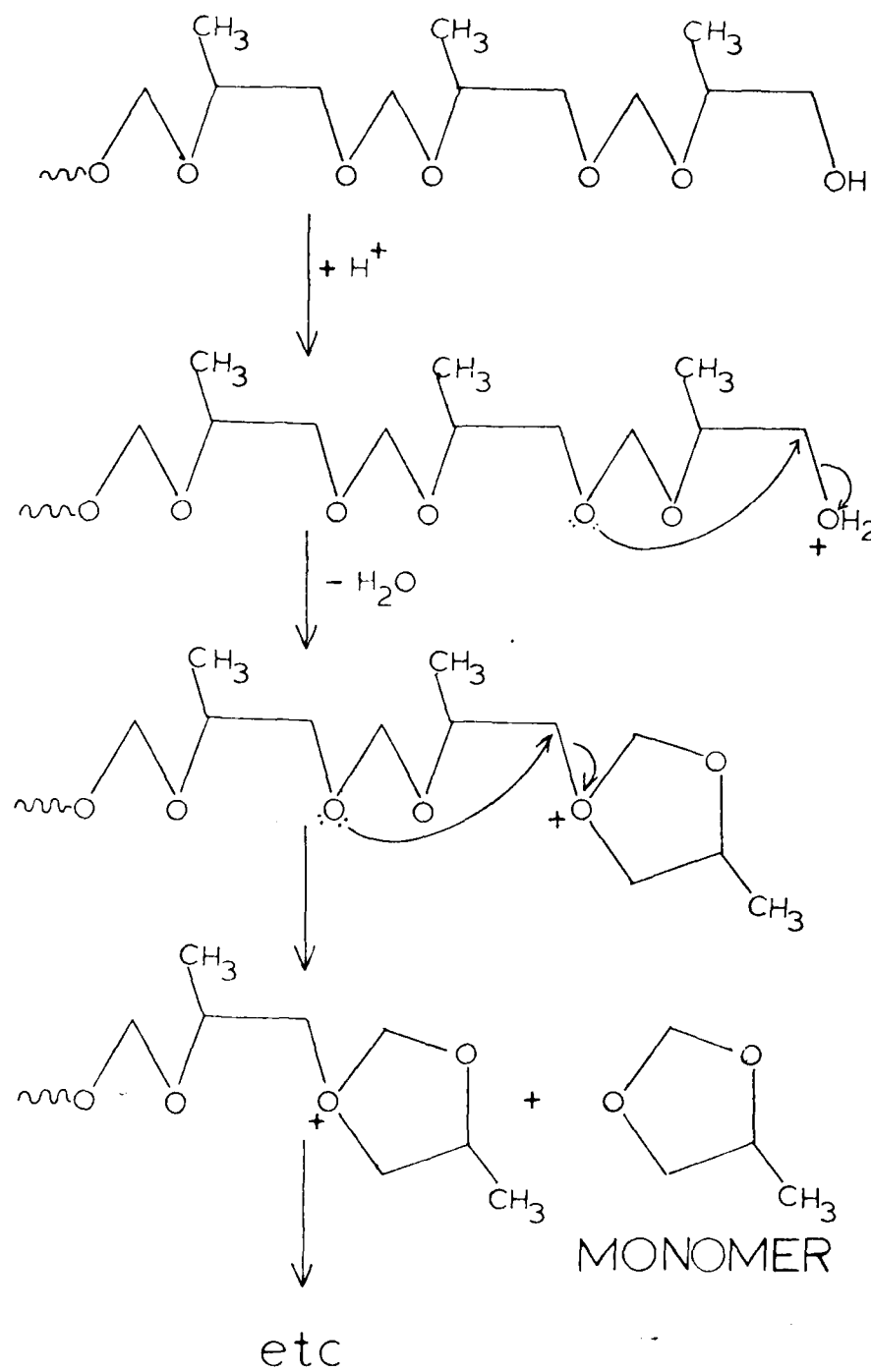
The facile acid catalyzed depolymerization of PMDO is undoubtedly attributable to initiation by protonation to form an oxonium ion. Protonation should occur equally probable with the terminal and internal oxygen atoms. However, since there are many more of the latter than the former we will discuss the processes involving the internal oxygens first (Scheme A).

The internal oxonium ion undergoes chain rupture into two fragments; the cyclic oxonium ion (III) and the shorter length hydroxymethyl derivative of PMDO (IV). The former being the propagating species is ready to unzip above the ceiling temperature of 8°. Loss of  $\text{CH}_2\text{O}$  from IV produces the stable dihydroxy terminated PDMO which will not decompose until reactivated by protonation. In a chain of N monomer units long, on the average one chain scission will lead to N/2 monomers; the average chain length of V will therefore be N/2.

Acidolysis of the terminal oxygen atom is depicted in Scheme B. In this process the entire PMDO chain was depolymerized.

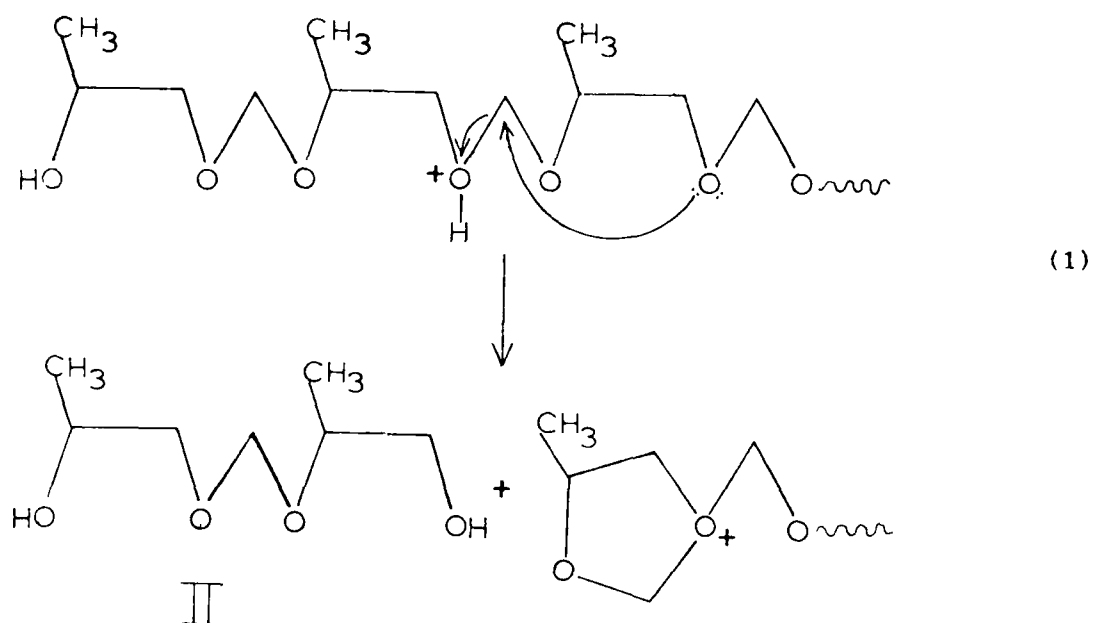


Scheme A. Mechanism of acidolysis of PMDO by protonation of inner oxygen atom.

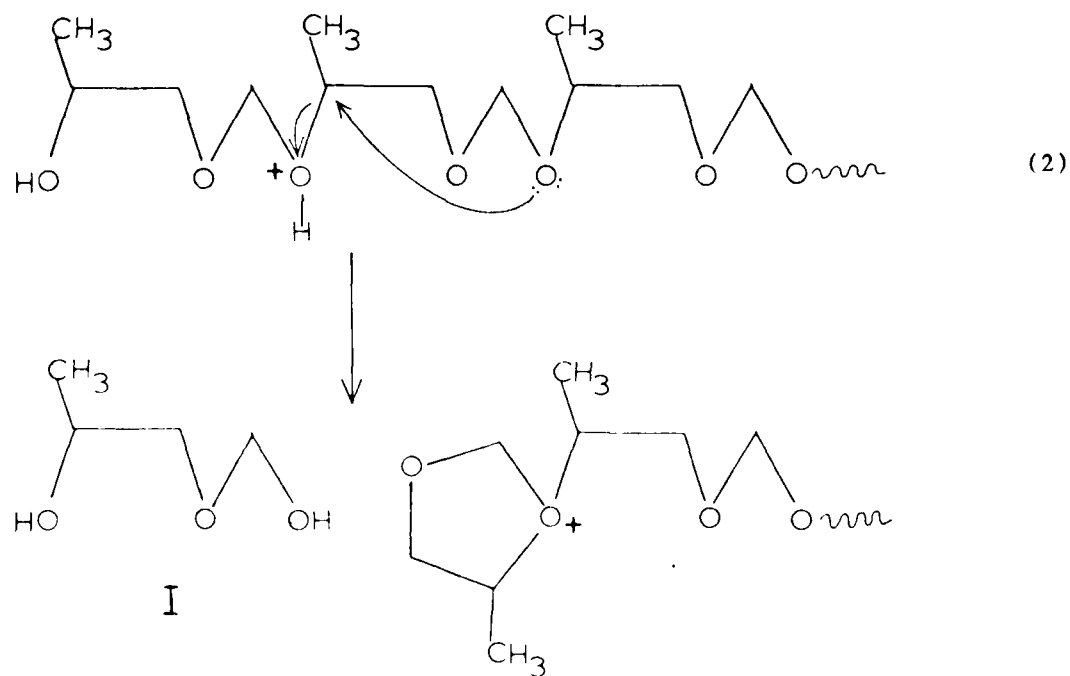


Scheme B. Mechanism of acidolysis of PDMO by protonation of terminal oxygen atom.

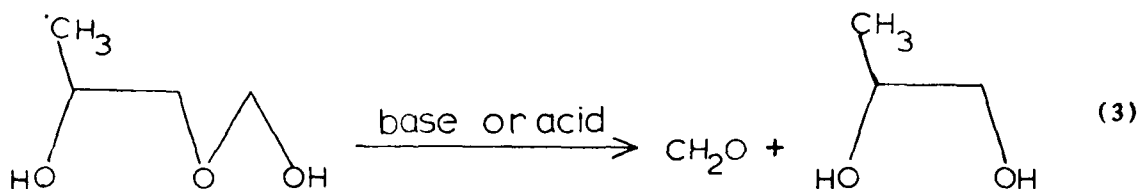
Minor product II and its isomer can be produced by the following rearrangement reaction of the oxonium ion.



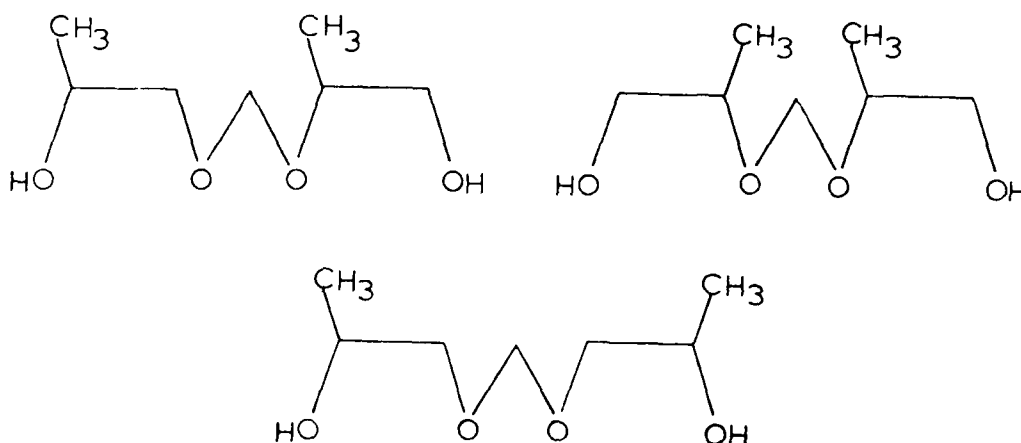
The other product I and its isomers can be formed by,



I is a hemiacetal and may be expected to decompose.



However, we search for but failed to detect any propan-1,2-diol. The three structural isomers of II are



The acidolysis of PMDO are therefore analogous to those proposed for polyaldehyde,<sup>8,9</sup> and poly-1,3-dioxolane.<sup>10</sup> The rate constant of acidolysis (Table II) was plotted according to Arrhenius relationship (Figure 5). The activation energy is ca. 8.5 kcal mole<sup>-1</sup>, which is much smaller than a value<sup>2</sup> of ca. 17 kcal mole<sup>-1</sup> estimate for the acidolysis of poly(1,3-dioxolane). Therefore, PMDO should undergo acid catalyzed decomposition more readily than PDO as mentioned in the Introduction.

#### Acknowledgement

The research was supported by a grant from ONR.

### References

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Captions for Figures

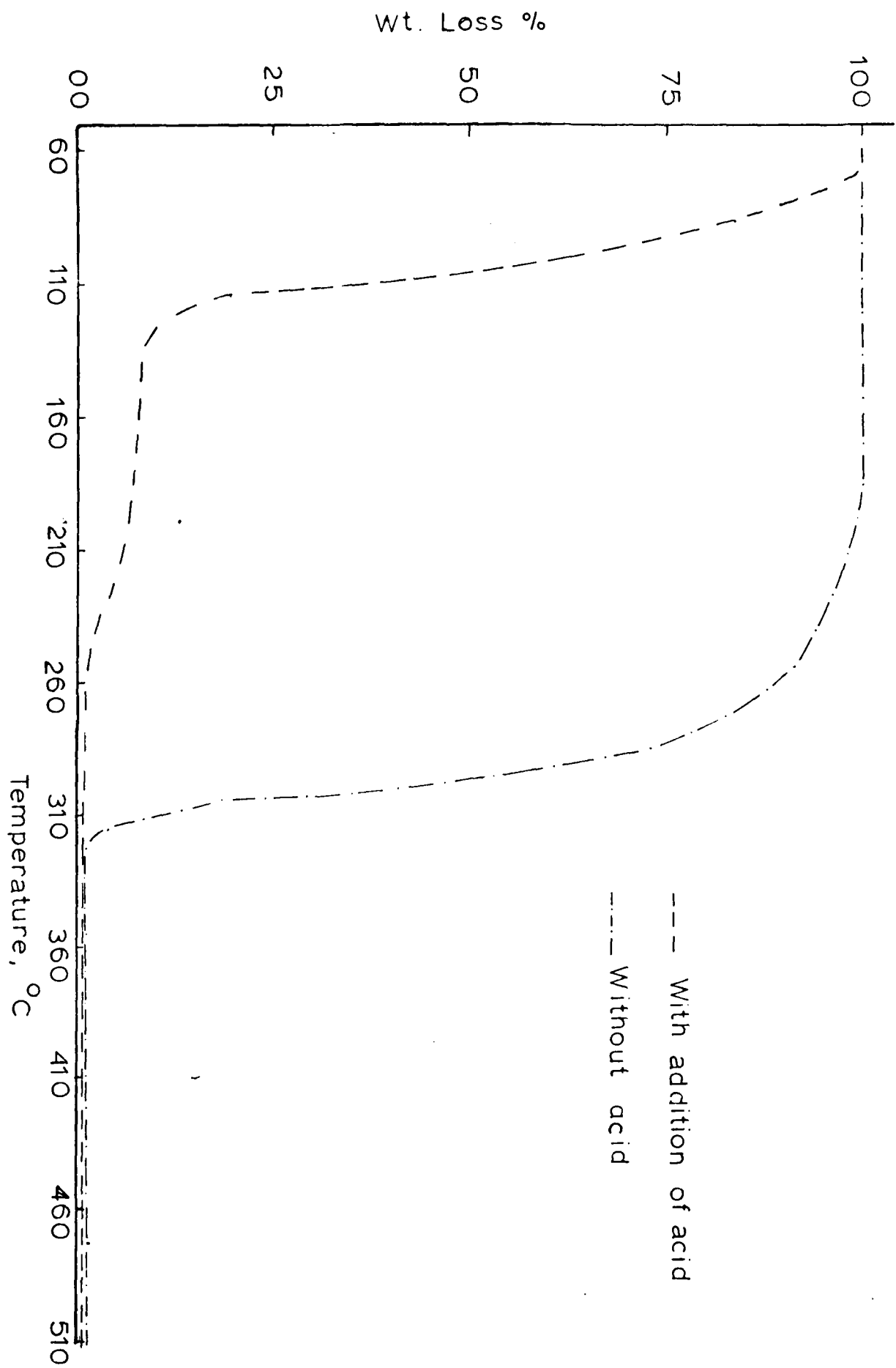
Figure 1 TGA curves of PMDO: (—) pure polymer (---) with 0.1 wt % TSA.

Figure 2 GPC curves for PMDO after reaction with 1 wt % TSA for (a) 0 min; (b) 15 min; (c) 30 min; (d) 60 min.

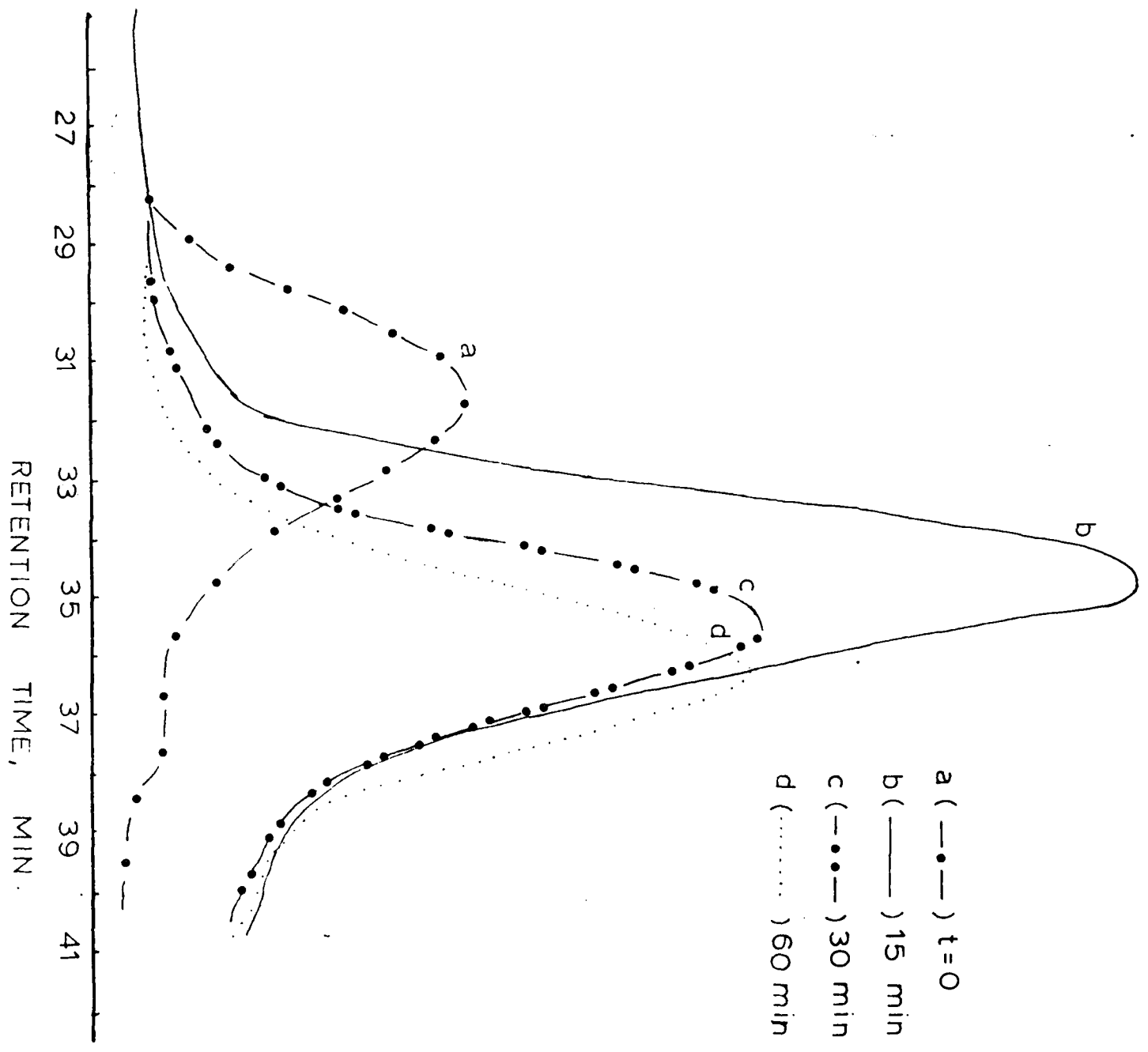
Figure 3 GPC curves for PMDO after reaction with 1 wt % TSA for (a) 90 min; (b) 120 min; (c) 150 min; (d) 1440 min.

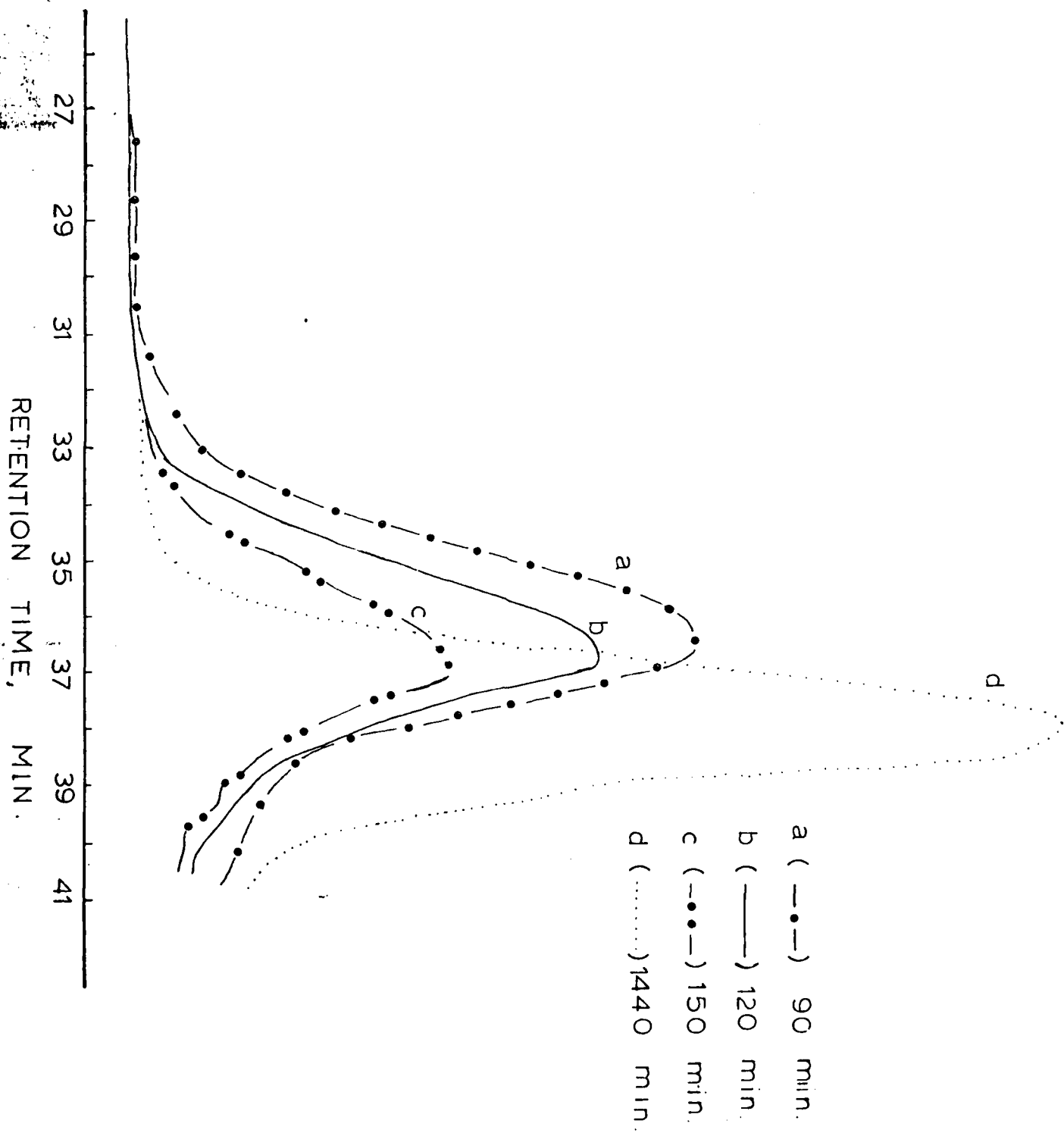
Figure 4 GC chromatogram of acidolysis products of PMDO.

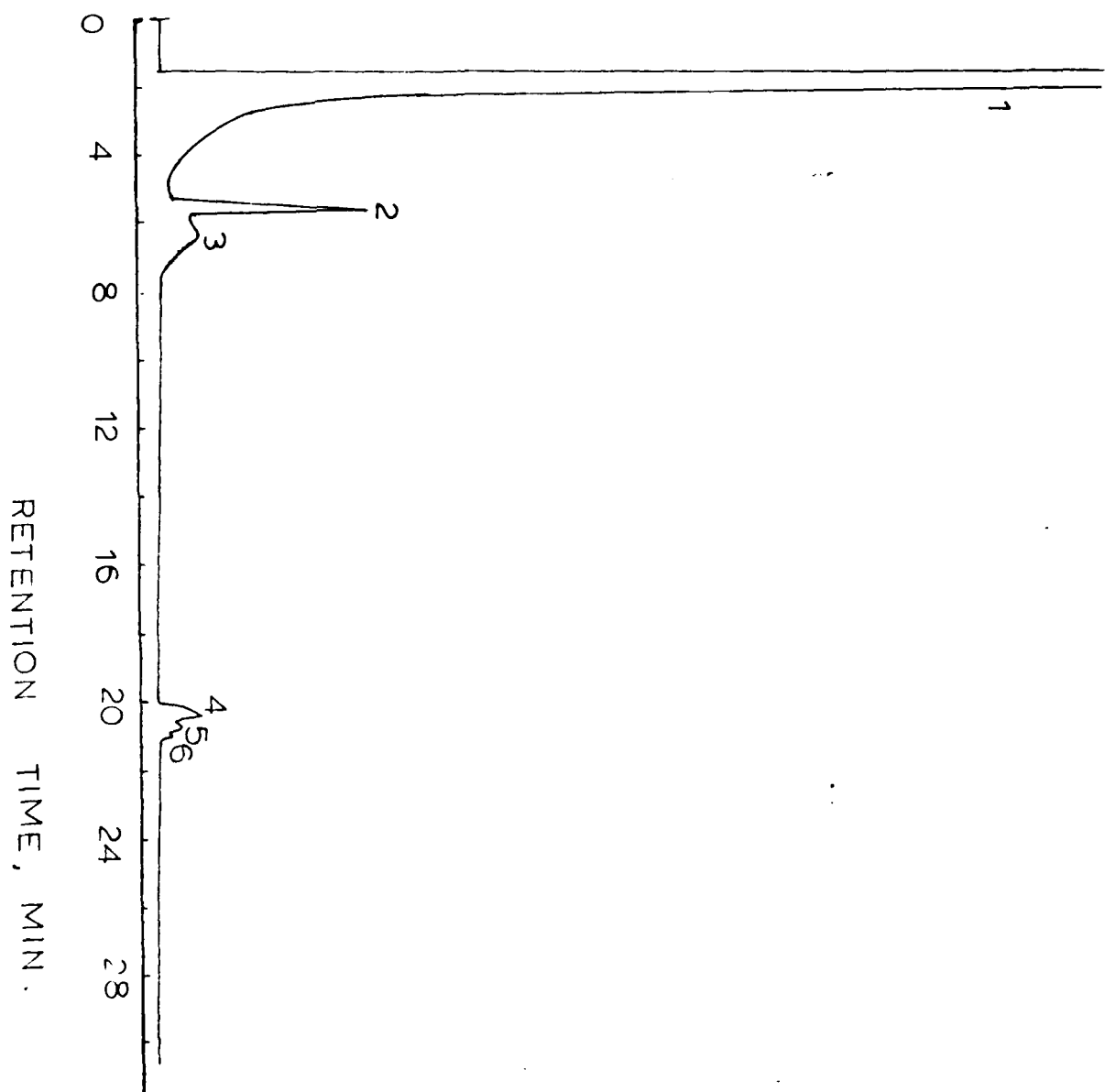
Figure 5 Arrhenius plot of the first order rate constants of acidolysis of PMDO.

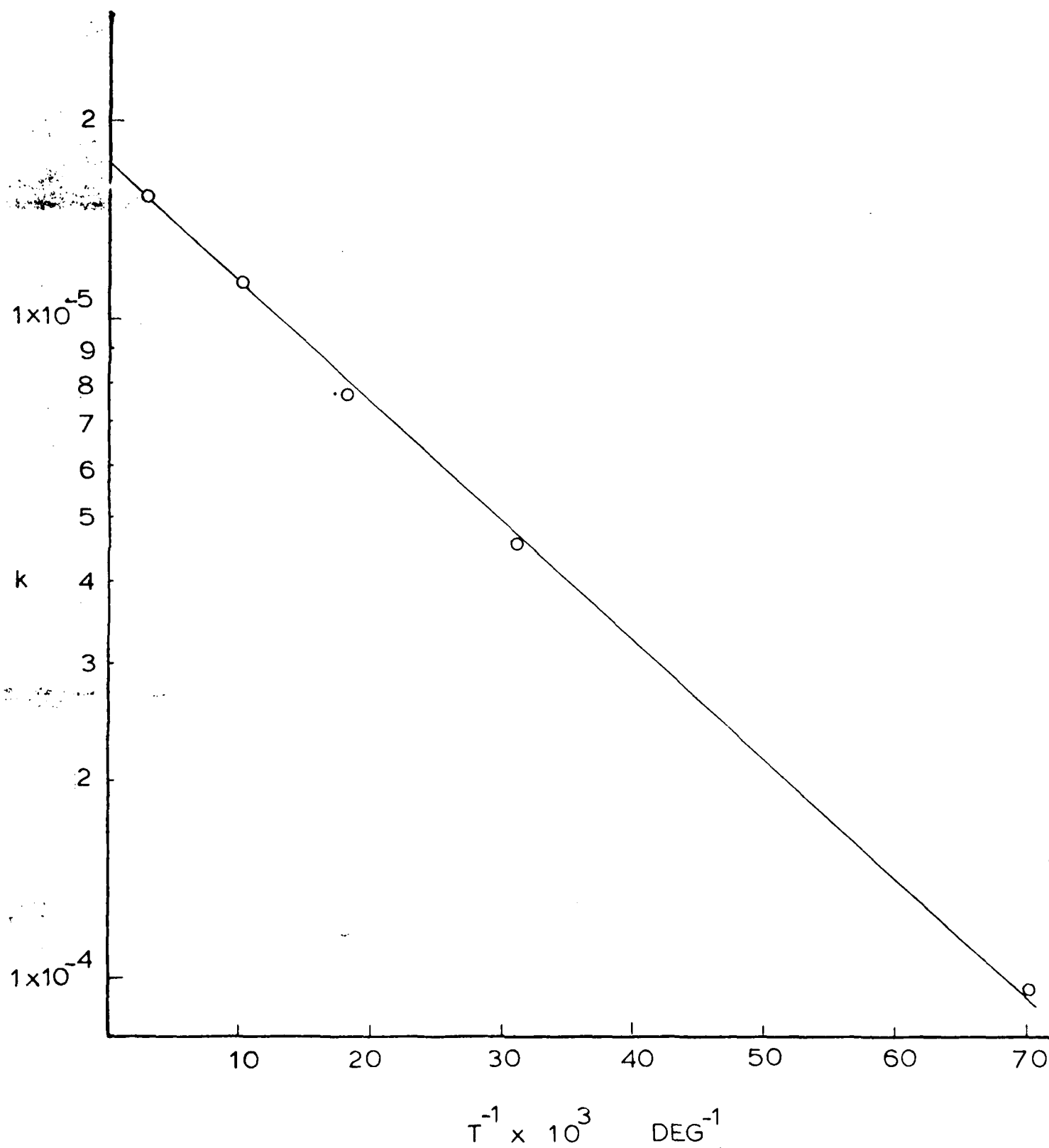


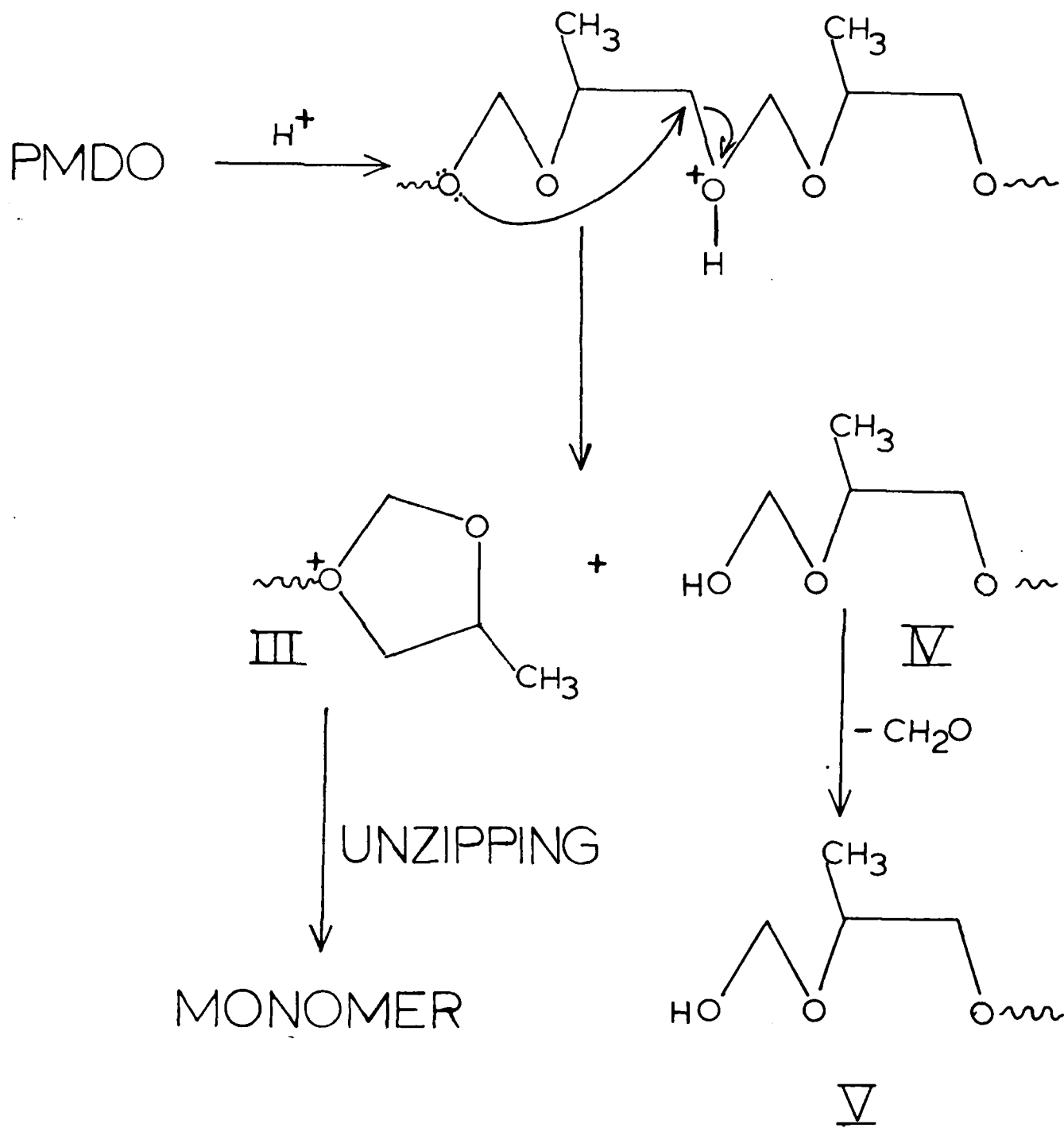
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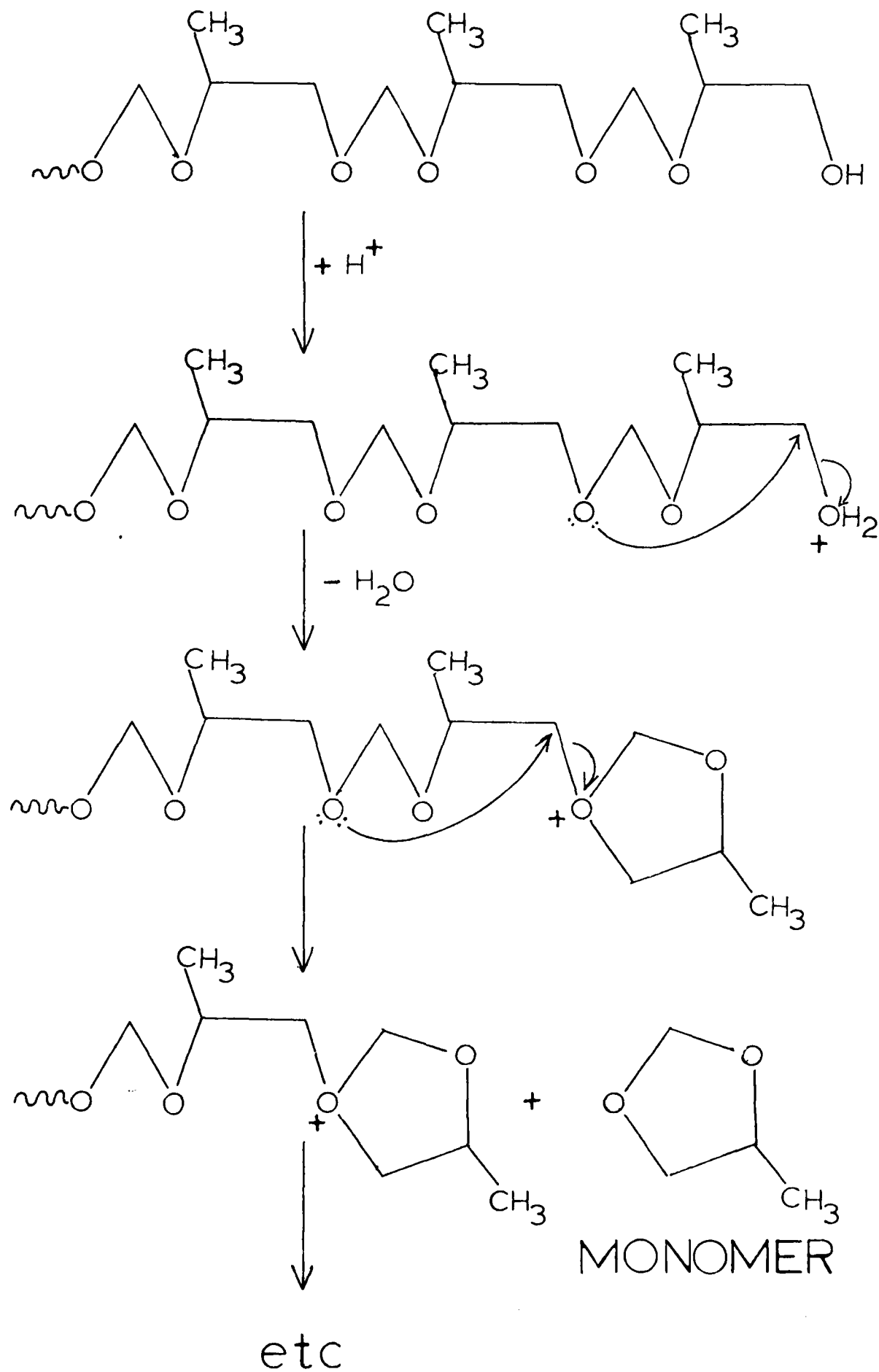






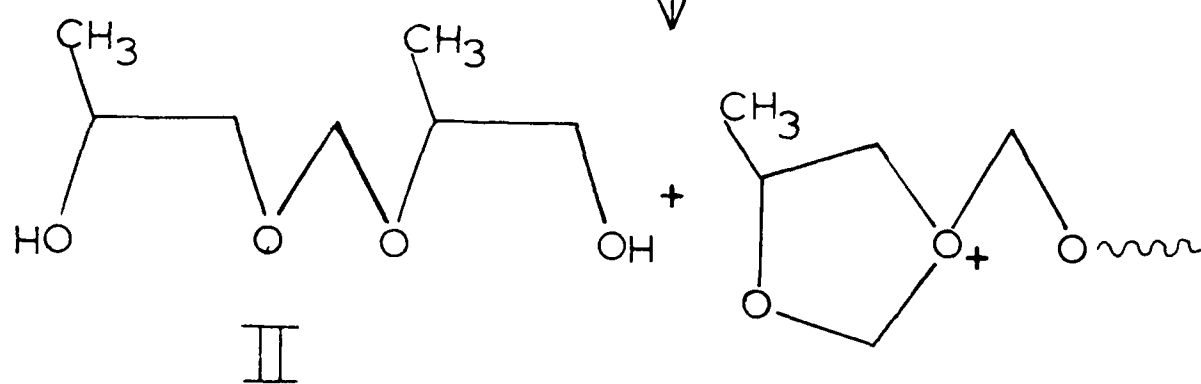
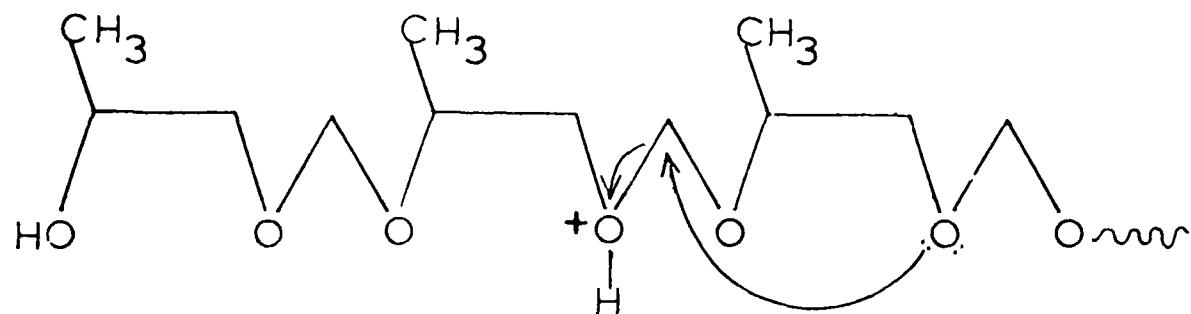


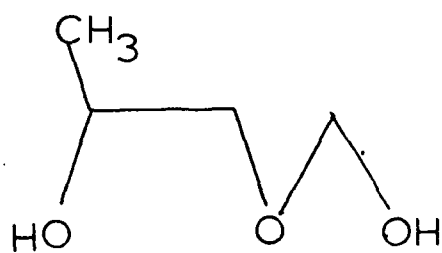
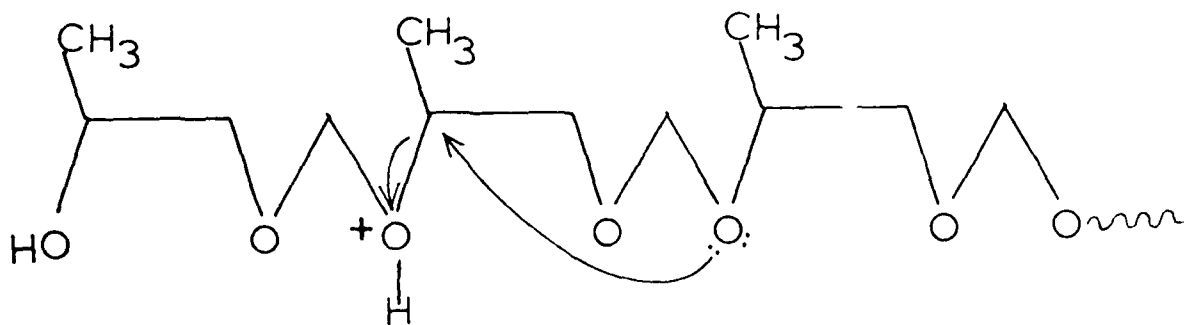
SCHEME 1. MECHANISM OF ANALYSIS OF  
 PMDO BY PROTONATION OF INTERNAL OXYGEN ATOM.



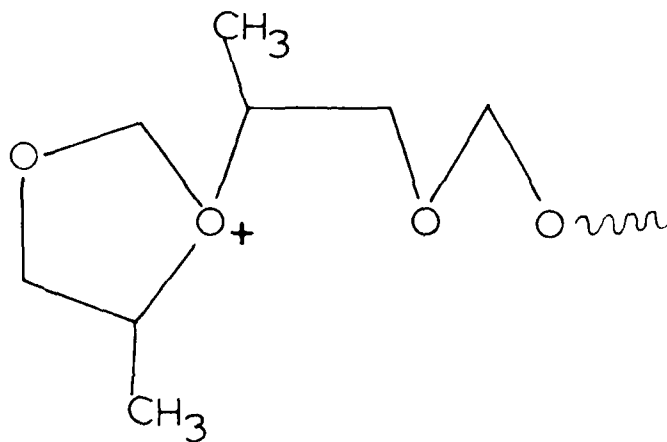
Scheme 1: Acid-catalyzed cleavage of polyacetal polymer into monomer



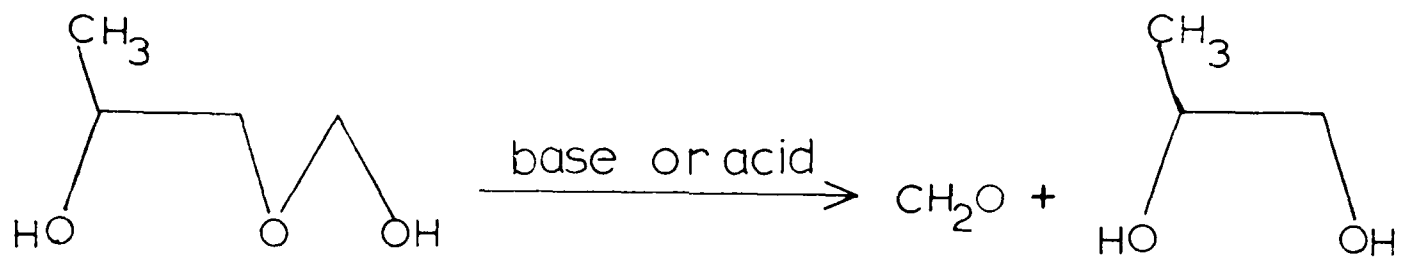


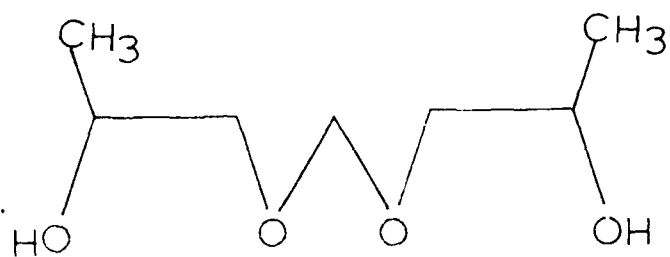
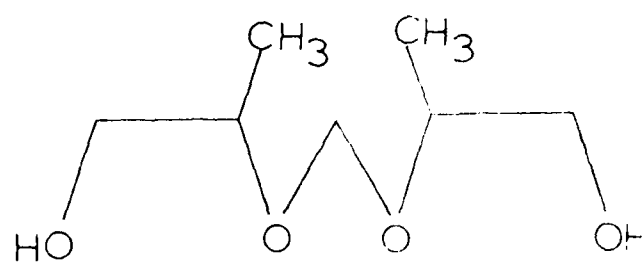
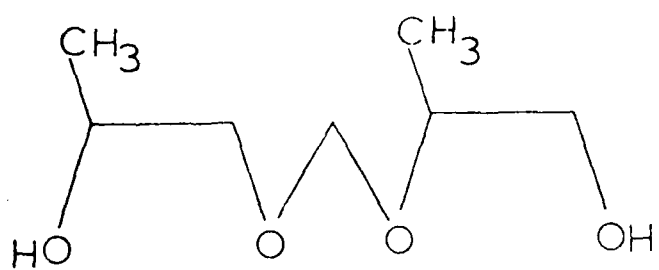


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